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(54) Title: OPTICAL FIBER COATINGS (57) Abstract <p>A curable resin composition for optical fiber coating exhibiting excellent stability in the liquid state and producing cured products having low tendency to stick in spite of its low Young's modulus. The composition is suitable for use as a coating material requiring a low Young's modulus. The composition, preferably comprises (1) 30-80 parts by weight of urethane (meth)acrylate obtained by reacting (A) a polyol compound, (B) a polyisocyanate compound, and (C) a hydroxyl group-containing (meth)acrylate compound, (2) 0.01-10 parts by weight of a polydimethylsiloxane compound which contains a urethane bond and a (meth)acryloyl group in the molecule, and (3) 10-70 parts by weight of a polymerizable diluent containing a polymerizable monofunctional vinyl monomer which can copolymerize with the component (1) and component (2), provided that the total of the component (1), component (2), and component (3) is 100 parts by weight.</p>		

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OPTICAL FIBER COATINGS5 Field of the Invention:

The present invention relates to optical fiber coatings and to a curable resin composition which exhibits excellent stability and produces a cured product having a low tackiness, which is manifested by
10 a low tendency to stick to itself, and a low Young's modulus.

Background of the Invention

In the production of optical fibers, a resin is
15 coated for protection and reinforcement immediately after spinning the molten glass fibers. A known two layer structure of the coating consists of a primary coating layer of a flexible resin which is coated onto the surface of optical fibers and a secondary coating
20 layer of a rigid resin which is provided over the primary coating layer. In certain cases, it may be useful to apply only one coating (a so-called single coating) which characteristics balance primary and secondary coatings to the extent possible. A so-called
25 optical fiber ribbon is known in the art in the application of optical fibers provided with resin coating. The optical fiber ribbon is made from several elemental optical fibers, e.g. four or eight optical fibers, by arranging these fibers in a plane and
30 securing them with a binder to produce a ribbon

structure with a rectangular cross section. A resin composition for forming the primary coating layer is called a soft coating, a resin composition for forming the secondary coating layer is called a hard coating, a material for producing the optical fiber ribbon structure from several optical fibers is called a ribbon matrix material. In addition, a material for further binding several optical fiber ribbons to produce multi-core optical fiber ribbons is called a bundling material.

Characteristics required for curable resins used as the coating materials for optical fibers include: being a liquid at ordinary temperatures and having a sufficiently low viscosity to be excellently coated; providing good productivity at a high cure speed; having sufficient strength and superior flexibility; exhibiting very little physical change during temperature changes over a wide range; having superior heat resistance and superior resistance to hydrolysis; showing superior reliability with little physical changes over time; showing superior resistance to chemicals such as acids and alkalis; exhibiting low moisture and water absorption; exhibiting superior light resistance; exhibiting high resistance to oils; and producing little hydrogen gas which adversely affects optical fiber characteristics.

Optical fibers with a resin coated thereon are wound through a capstan or pulley on a production line. During production, optical fibers must be wound and rewound smoothly without the coating of the optical fiber sticking to the coating of another portion of the same optical fiber or coated optical fiber, or to

winding parts, such as pulleys or the like. Various different properties are required for resin coating according to the parts where the resin coating is applied.

5 An object of the present invention is to provide a single coating, ink coating or secondary coating, for optical fibers, preferably optical glass fibers having a low tackiness.

 Another object of the present invention is
10 to provide a liquid curable resin composition which produces a cured product having a low tackiness or tendency to stick to itself and a low Young's modulus.

 A further object of the present invention is to provide a liquid curable resin composition that
15 has a low tackiness and a low Young's modulus and can be formulated as a colored or uncolored outer primary coating, or an ink coating for use on optical fibers and/or in optical fiber ribbon.

20 Summary of the Invention

 One or more of the above objects can be achieved by an optical fiber having a coating, which coating before curing is a curable resin composition of the present invention which comprises: (A) a urethane
25 (meth)acrylate oligomer; (B) a urethane (meth)acryloyl polysiloxane compound; and (C) a polymerizable vinyl monomer.

Detailed Description Of A Preferred Embodiment

30 A preferred embodiment of the present invention is a curable resin composition adapted for

use as a single coating, a secondary coating or ink coating comprising: (1) 30-80 parts by weight of urethane (meth)acrylate oligomer obtained by reacting (A) a polyol compound, (B) a polyisocyanate compound, and (C) a hydroxyl group-containing (meth)acrylate compound, (2) 0.01-10 parts by weight of a urethane (meth)acryloyl polysiloxane compound which contains a urethane bond and a (meth)acryloyl group in the molecule, and (3) 10-70 parts by weight of a polymerizable diluent, particularly containing a polymerizable monofunctional vinyl monomer which can copolymerize with the component (1) and component (2), provided that the total of the component (1), component (2), and component (3) is 100 parts by weight.

It is preferred that the curable resin composition can produce a cured product with a Young's modulus of 10 kg/mm² or less at 23°C when cured with radiation or heat. In another preferred embodiment, cured films made from the liquid curable resin composition exhibits 50 g/cm or less as a T-peel strength at the interface of two sheets of such films when the two sheets are layered in a way that the cured surfaces of the two films are in contact with each other.

The above object is further achieved in the present invention by a cured product produced from this liquid curable resin composition.

The present invention will now be explained in detail.

The urethane (meth)acrylate (1) used in the

present invention can be prepared by reacting (A) a polyol compound, (B) a polyisocyanate compound, and (C) a hydroxyl group-containing (meth)acrylate compound.

Exemplary processes for for reacting these
5 compounds include (i) a process for reacting the polyol compound (A), the polyisocyanate compound (B), and the hydroxyl group-containing (meth)acrylate compound (C) together; (ii) a process for reacting the polyol
10 compound (A) and the polyisocyanate compound (B), and reacting the resulting product with the hydroxyl group-containing (meth)acrylate compound (C); (iii) a process for reacting the polyisocyanate compound (B) and the hydroxyl group-containing (meth)acrylate compound (C), and reacting the resulting product with the polyol
15 compound (A); and (iv) a process for reacting the polyisocyanate compound (B) and the hydroxyl group-containing (meth)acrylate compound (C), reacting the resulting product with the polyol compound (A), and reacting again the hydroxyl group-containing
20 (meth)acrylate compound (C).

Polyols suitable for use as the component (A) include polyether diols, polyester diols, polycarbonate diols, polycaprolactone diols, and the like. These polyols may be used either individually or
25 in combinations of two or more. There are no specific limitations to the manner of polymerization of the structural unit in these polyols. Any of random polymerization, block polymerization, or graft polymerization is acceptable.

30 Exemplary polyether diols include polyethylene glycol, polypropylene glycol,

polytetramethylene glycol, polyhexamethylene glycol, polyheptamethylene glycol, polydecamethylene glycol, and polyether diols obtained by ring-opening copolymerization of two or more ion-polymerizable cyclic compounds. Here, included in examples of the ion-polymerizable cyclic compound are cyclic ethers, such as ethylene oxide, propylene oxide, butene-1-oxide, isobutene oxide, 3,3-bis(chloromethyl)oxetane, tetrahydrofuran, 2-methyltetrahydrofuran, 3-methyltetrahydrofuran, dioxane, trioxane, tetraoxane, cyclohexene oxide, styrene oxide, epichlorohydrin, glycidyl methacrylate, allyl glycidyl ether, allyl glycidyl carbonate, butadiene monoxide, isoprene monoxide, vinyl oxetane, vinyl tetrahydrofuran, vinyl cyclohexene oxide, phenyl glycidyl ether, butyl glycidyl ether, and benzoic acid glycidyl ester. Examples of the combination of two or more ion-polymerizable cyclic compounds include combinations for producing a binary copolymer, such as tetrahydrofuran and propylene oxide, tetrahydrofuran and 2-methyltetrahydrofuran, tetrahydrofuran and 3-methyltetrahydrofuran, tetrahydrofuran and ethylene oxide, and butene-1-oxide and ethylene oxide, combinations for producing a ternary copolymer such as a combination of tetrahydrofuran, butene-1-oxide, and ethylene oxide, and a combination of tetrahydrofuran, butene-1-oxide, and ethylene oxide. Moreover, polyether diols obtained by ring-opening copolymerization of one of the above-mentioned ion-polymerizable cyclic compounds and a cyclic imine such as ethyleneimine, a cyclic lactone acid such as β -propiolactone or glycolic

acid lactide, or a dimethylcyclopolysiloxane, can also be used. The ring-opening copolymers of these ion-polymerizable cyclic compounds may be either random copolymers or block copolymers.

5 Suitable commercial polyether diols products are available under the trade names PTMG1000, PTMG2000 (manufactured by Mitsubishi Chemical Corp.), PPG1000, EXCENOL2020, 1020, (manufactured by Asahi Oline Co., Ltd.), PEG1000, Unisafe DC1100, DC1800
10 (manufactured by Nippon Oil and Fats Co., Ltd.), PTG1000, PTG2000, PTG3000, PPTG2000, PPTG1000, PTGL1000, PTGL2000 (manufactured by Hodogaya Chemical Co., Ltd.), and Z-3001-4, Z-3001-5, PBG2000A, PBG2000B (manufactured by Daiichi Kogyo Seiyaku Co., Ltd.).

15 Polyester diols obtained by the reaction of a polyhydric alcohol and a polybasic acid are given as examples of the polyester diols. As examples of the polyhydric alcohol, ethylene glycol, polyethylene glycol, propylene glycol, polypropylene glycol,
20 tetramethylene glycol, polytetramethylene glycol, 1,6-hexanediol, neopentyl glycol, 1,4-cyclohexanedimethanol, 3-methyl-1,5-pentane diol, 1,9-nonane diol, and 2-methyl-1,8-octane diol can be given. As examples of the polybasic acid, phthalic acid,
25 isophthalic acid, terephthalic acid, maleic acid, fumaric acid, adipic acid, and sebacic acid can be given.

 These polyester diol compounds are commercially available under the trade names Kurapol P-
30 2010, P-1010, L-2010, L-1010, A-2010, A-1010, P-2020, F-1010, PMIPA-2000, PKA-A, PNOA-2010, and PNOA-1010

(manufactured by Kuraray Co., Ltd.).

Examples of suitable polycarbonate diols include polycarbonate of polytetrahydrofuran, poly(hexanediol carbonate), poly(nonanediol carbonate),
5 and poly(3-methyl-1,5-pentamethylene carbonate) can be given.

As commercially available products among these polycarbonate diols, DN-980, DN-981, DN-982, DN-983 (manufactured by Nippon Polyurethane Industry Co.,
10 Ltd.), PMC-2000, PMC-1000, PNOC-2000, PNOC-1000 (manufactured by Kuraray Co., Ltd.), PLACCEL CD220, CD210, CD220PL, CD210PL, CD220HL, CD210HL (manufactured by Daicel Chemical Industries, Ltd.), PC-8000 (manufactured by PPG Co. of the U.S.), and PC-THF-CD
15 (manufactured by BASF) can be given.

Polycaprolactone diols obtained by the reaction of ϵ -caprolactone and a diol compound are given as examples of suitable polycaprolactone diols. Here, given as examples as the diol compound are
20 ethylene glycol, polyethylene glycol, propylene glycol, polypropylene glycol, tetramethylene glycol, polytetramethylene glycol, 1,2-polybutylene glycol, 1,6-hexanediol, neopentyl glycol, and 1,4-cyclohexanedimethanol, 1,4-butanediol.

25 Commercially available products among these polycaprolactone diols include PLACCEL 240, 230, 230ST, 220, 220ST, 220NP1, 212, 210, 220N, 210N, L230AL, L220AL, L220PL, L220PM, and L212AL (all manufactured by Daicel Chemical Industries, Ltd.).

30 Other suitable polyols other than those mentioned above which can be used as the component (A)

are ethylene glycol, propylene glycol, 1,4-butanediol, 1,5-pentane diol, 1,6-hexanediol, neopentyl glycol, 1,4-cyclohexanedimethanol, hydrogenated bisphenol A, hydrogenated bisphenol F, dimethylol compound of
5 dicyclopentadiene, tricyclodecanedimethanol, pentacyclopentadecanedimethanol, ring-opening polymerization compounds of β -methyl- δ -valerolactone, polybutadiene terminated at hydroxy group, hydrogenated polybutadiene terminated at hydroxy group, castor oil-
10 modified diol, polydimethylsiloxane terminated at hydroxyl group, and diols modified with polydimethylsiloxane carbitol.

Diamines can also be used together with the above-mentioned polyols. As such diamines,
15 ethylenediamine, tetramethylenediamine, hexamethylenediamine, p-phenylenediamine, 4,4'-diaminodiphenylmethane, diamines including a hetero atom, polyether diamines, and the like can be given.

The molecular weight of these polyol
20 compounds, in terms of polystyrene-reduced number average molecular weight, is usually from 50 to 15,000, and preferably from 1,000 to 3,000.

Examples of suitable polyisocyanate compounds that may be used as the component (B) include
25 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, 1,3-xylylene diisocyanate, 1,4-xylylene diisocyanate, 1,5-naphthalene diisocyanate, m-phenylene diisocyanate, p-phenylene diisocyanate, 3,3'-dimethyl-4,4'-diphenylmethane diisocyanate, 4,4'-diphenylmethane
30 diisocyanate, 3,3'-dimethylphenylene diisocyanate, 4,4'-biphenylene diisocyanate, 1,6-hexane diisocyanate,

isophorone diisocyanate, methylenebis(4-cyclohexylisocyanate), 2,2,4-trimethylhexamethylene diisocyanate, bis(2-isocyanatethyl)fumarate, 6-isopropyl-1,3-phenyl diisocyanate, 4-diphenylpropane diisocyanate, hydrogenated diphenylmethane diisocyanate, hydrogenated xylylene diisocyanate, tetramethyl xylylene diisocyanate, and lysine isocyanate. These polyisocyanate compounds may be used either individually or in combinations of two or more.

The following compounds are given as examples of the hydroxyl group-containing (meth)acrylate useful as the component (C): (meth)acrylates such as 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 2-hydroxybutyl (meth)acrylate, 2-hydroxy-3-phenyloxypropyl (meth)acrylate, 1,4-butanediolmono(meth)acrylate, 2-hydroxyalkyl (meth)acryloyl phosphate, 4-hydroxycyclohexyl (meth)acrylate, 1,6-hexanediol mono(meth)acrylate, neopentyl glycol mono(meth)acrylate, trimethyloolpropane di(meth)acrylate, trimethylolethane di(meth)acrylate, pentaerythritol tri(meth)acrylate, dipentaerythritol penta(meth)acrylate, (meth)acrylate compounds shown by the following formula (1) or (2),



wherein R^1 is a hydrogen atom or a methyl group and n

denotes an integer from 1 to 15. The compounds obtained by the addition reaction of a glycidyl group-containing compound, such as alkyl glycidyl ether, allyl glycidyl ether, or glycidyl (meth)acrylate, and (meth)acrylic acid can also be used. These hydroxyl group-containing (meth)acrylates may be used either individually or in combinations of two or more.

The ratio of the polyol (A), polyisocyanate compound (B), and hydroxyl group containing (meth)acrylate (C) used for preparing the urethane (meth)acrylate (1) is determined so that for one equivalent of the hydroxyl group included in the polyol compound, 1.1 to 3 equivalent of isocyanate group included in the polyisocyanate compound and 0.1 to 1.5 equivalent of the hydroxyl group included in the hydroxyl group-containing (meth)acrylate compounds are used.

In the reaction of these three components, a urethanization catalyst, such as copper naphthenate, cobalt naphthenate, zinc naphthenate, di-n-butyl tin dilaurate, triethylamine, or triethylenediamine-2-methyltriethylene-amine, is usually used in an amount of 0.01 to 1 wt% of the total amount of the reactants. The reaction is carried out at a temperature of 10 to 90°C, preferably 30 to 80°C.

The number average molecular weight of the urethane (meth)acrylate (1) used in the present invention is preferably in the range from 100 to 20,000, more preferably from 500 to 15,000, and more in particular between 1000-5000. If the number average molecular weight of the urethane (meth)acrylate is less

than 100, the Young's modulus of the resulting cured products tends to increase; if the number average molecular weight is larger than 20,000, on the other hand, the viscosity of the composition becomes high, making it difficult to handle the composition.

The amount of the urethane (meth)acrylate used in the composition of the present invention is 30 to 80 wt% of the total amount of the components (1), (2), and (3). The amount of 40 to 70 wt% is particularly preferred to ensure excellent applicability when the composition is applied to optical fibers, flexibility of the coating material after curing, and superior reliability of the products. If the amount of the urethane (meth)acrylate (1) is less than 30 wt%, toughness of the resulting composition decreases; if greater than 80 wt%, the viscosity of the composition increases, making it difficult to handle the composition.

The urethane (meth)acryloyl polysiloxane compound which contains a urethane bond and (meth)acryloyl group in the molecule used as the component (2) in the present invention can be prepared, for example, by reacting a polyisocyanate compound, a later-described reactive silicone compound which possesses a hydroxyl group at at least one of the terminals, and a hydroxyl group-containing (meth)acrylate compound.

Here, as the polyisocyanate compounds and the hydroxyl group-containing (meth)acrylate compounds, the same polyisocyanate compounds and the hydroxyl group-containing (meth)acrylate compounds described

above relating to the component (1) can be used.

The polysiloxane structure in the polysiloxane compound used in the present invention is introduced using a silicone compound which contains a hydroxyl group at at least one of the terminals and an
5 non-reactive organic group at another terminal.

The polysiloxane compound can be a known type of siloxane, for example polydimethylsiloxane, polydiethylsiloxane, polydiphenylsiloxane,
10 polydimethyldiphenylsiloxane and other combinations of alkyl and/or aryl groups. It is preferred to use polydimethylsiloxanes.

A silicone compound having a hydroxyl group at one of the terminals is given as an example of such
15 a silicone compound. A typical example is polydimethylsiloxane having an organic group, such as 3-(2'-hydroxyethoxy)propyl group, 3-(2',3'-hydroxypropyloxy)propyl group, 3-(2'-ethyl-2'-hydroxymethyl-3-hydroxy)propyl group, or 3-(2'-hydroxy-
20 3'-isopropylamino)propyl group, at one of the terminals, and a non-reactive organic group, such as trimethylsilyloxy group, at another terminal.

Given as specific examples of silicone compounds having hydroxyl group on one terminal are
25 α -{3-(2'-hydroxyethoxy) propyl}- ω -trimethylsilyloxy-polydimethylsiloxane, α -{3-(2'-hydroxyethoxy)propyl}- ω -trimethylsilyloxypolyethylenediphenyl siloxane, α -{3-(2',3'-dihydroxypropyloxy)propyl}- ω -trimethylsilyloxypolydimethylsiloxane, α -{3-(2',3'-dihydroxy-
30 propyloxy)propyl}- ω -trimethylsilyloxypolyethylenediphen

ylsiloxane, α -{3-(2'-ethyl-2'-hydroxymethyl-3-hydroxy)-propyl}- ω -trimethyl-silyloxypolydimethylsiloxane, α -{3-(2'-ethyl-2'-hydroxymethyl-3-hydroxy)propyl}- ω -trimethylsilyloxy-polyethylenediphenyl siloxane, 5 α -{3-(2'-hydroxy-3'-isopropylamino)propyl}- ω -trimethylsilyloxypolydimethylsiloxane, and α -{3-(2'-hydroxy-3'-isopropylamino)propyl}- ω -trimethylsilyloxypolyethylene-diphenyl siloxane.

This type of silicone compound having a 10 hydroxyl group attached to at least one molecular terminal is commercially available under trademarks such as Silaplane FM-0411, FM-0413, FM-0415, FM0421, FM-0425, FM-D411, FM-D421, FM-D425 (manufactured by Chisso Corp.) and Shin-Etsu Silicone X-22-170A, 15 X-22-170B, X22-170D, X-22-176B, X-22-176D, X-22-176DX, X-22-178A, X-22-178B (manufactured by Shin-Etsu Chemical Co., Ltd.).

Preferred examples of commercially available products of dimethylsilicone compound 20 containing a hydroxyl group at one of the terminals include silaplane FM-0411, FM-0421, FM-0425, FM-D411, FM-D421, FM-D425 (manufactured by Chisso Corp.), TSL9105 (manufactured by Toshiba Silicone Co., Ltd.), and X-22-170A, X-22-170B, X-22-170D, X-22-176B, X-22- 25 176D, X-22-176DX, X-22-178A, X-22-178B (manufactured by Shin-Etsu Silicone Co., Ltd.).

These polysiloxane compounds can be prepared, for example, by a process of reacting the hydroxyl group-containing silicone compound, 30 polyisocyanate compound, and hydroxyl group-containing

(meth)acrylate together; a process comprising reacting the silicone compound and polyisocyanate compound, and reacting the resulting product with the hydroxyl group-containing (meth)acrylate; a process comprising
5 reacting hydroxyl group-containing (meth)acrylate and polyisocyanate compound, and reacting the resulting product with the silicone compound. The proportion of the reactants in these processes is preferably determined so that the total amount of the hydroxyl
10 groups in the hydroxyl group-containing silicone compound and the hydroxyl group-containing (meth)acrylate is approximately equivalent to the amount of the isocyanate group in the polyisocyanate compound.

15 A structure such as a polyurethane polyol structure can be introduced between the polysiloxane structure and the (meth)acryloyl group by adding a polyol to the starting materials in these reactions. The compounds previously given in the illustration of
20 the component (1) can be used as the polyol in these reactions. These polyol compounds may be used either individually or in combinations of two or more.

The process for obtaining the polysiloxane compound having a polyol structure includes a process
25 of reacting the hydroxyl group-containing silicone compound, polyol, polyisocyanate compound, and hydroxyl group-containing (meth)acrylate altogether; a process comprising reacting the polyol and polyisocyanate, and reacting the resulting product with the silicone
30 compound and hydroxyl group-containing (meth)acrylate; a process comprising reacting the silicone compound,

polyisocyanate compound, and hydroxyl group-containing (meth)acrylate, and reacting the resulting compound with the polyol; a process comprising reacting the polyisocyanate compound and silicone compound, reacting
5 the resulting compound with the polyol, and finally with the hydroxyl group-containing (meth)acrylate; and a process comprising reacting the polyisocyanate and hydroxyl group containing (meth)acrylate, reacting the resulting compound with the polyol, and finally with
10 the silicone compound.

As mentioned above, the (meth)acryloyl group in the polysiloxane compound used in the present invention is introduced into only one of the terminals of the polysiloxane structure. The low tendency to
15 stick cannot be obtained if the (meth)acryloyl group is introduced into two or more terminals of the polysiloxane structure.

It is desirable that the polysiloxane compound (2) used in the present invention have a
20 polystyrene-reduced number average molecular weight in the range of 800 to 15,000, and particularly 1,000 to 7,000. If the number average molecular weight is less than 800, the cured products made from the composition containing this polysiloxane compound do not have
25 sufficiently low tendency to stick so that the products may adhered between themselves. If the number average molecular weight is more than 15,000, on the other hand, the liquid composition containing this compound may have impaired storage stability.

30 The amount of the polysiloxane compound used in the liquid curable resin composition of the

present invention is preferably from 0.01 to 10 wt%, preferably from 0.05 to 5 wt%, of the total amount of the components (1), (2), and (3). If the content of the polysiloxane compound is less than 0.01 wt%,
5 sufficiently low tendency to stick may not be obtained in the cured products; if more than 10 wt%, storage stability of the liquid resin composition may be impaired.

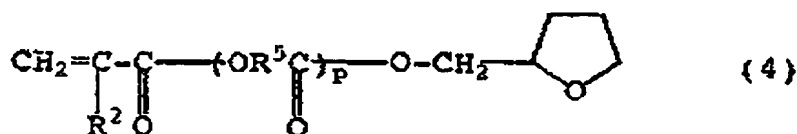
The component (3) of the present invention
10 is a polymerizable diluent which comprises a combination of a polymerizable monofunctional vinyl monomer containing at least one polymerizable vinyl group in the molecule and a polymerizable
polyfunctional vinyl monomer containing a plurality of
15 polymerizable vinyl groups in the molecule, both monofunctional and polyfunctional monomers being different from the monomers of the component (1) or component (2), but copolymerizable therewith.

Among the polymerizable diluent used as the
20 component (3) in the present invention, suitable examples of the polymerizable monofunctional vinyl monomers include vinyl monomers, such as N-vinyl pyrrolidone, N-vinyl caprolactam, vinyl imidazole, and vinyl pyridine; (meth)acrylates, such as
25 isobornyl(meth)acrylate, bornyl(meth)acrylate, tricyclodecanyl(meth)acrylate, dicyclopentanyl(meth)acrylate, dicyclopentenyl(meth)acrylate, cyclohexyl(meth)acrylate, benzyl(meth)acrylate, 4-butylcyclohexyl(meth)acrylate, acryloylmorpholine,
30 2-hydroxyethyl(meth)acrylate, 2-hydroxypropyl(meth)acrylate, 2-hydroxybutyl(meth)acrylate,

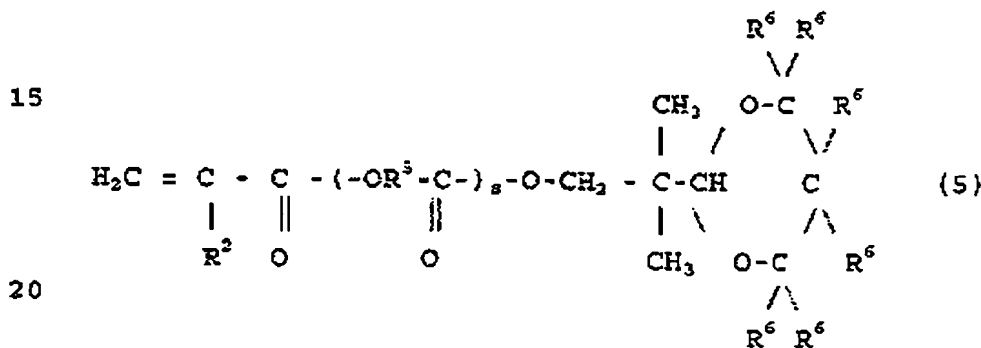
methylethyl(meth)acrylate, ethylethyl(meth)acrylate,
propylethyl(meth)acrylate, isopropylethyl(meth)acrylate,
butylethyl(meth)acrylate, amylethyl(meth)acrylate,
isobutylethyl(meth)acrylate, t-butylethyl(meth)acrylate,
5 pentylethyl(meth)acrylate, isoamylethyl(meth)acrylate,
hexylethyl(meth)acrylate, heptylethyl(meth)acrylate,
octylethyl(meth)acrylate, iso-octylethyl(meth)acrylate,
2-ethylhexylethyl(meth)acrylate, nonylethyl(meth)acrylate,
decylethyl(meth)acrylate, iso-decylethyl(meth)acrylate,
10 undecylethyl(meth)acrylate, dodecylethyl(meth)acrylate,
laurylethyl(meth)acrylate, stearylethyl(meth)acrylate, iso-
stearylethyl(meth)acrylate, tetrahydrofurfurylethyl(meth)-
acrylate, butoxyethyl(meth)acrylate, ethoxydiethylene
glycol(meth)acrylate, benzylethyl(meth)acrylate,
15 phenoxyethyl(meth)acrylate, polyethylene glycol
mono(meth)acrylate, polypropylene glycol
mono(meth)acrylate, methoxyethylene glycol
(meth)acrylate, ethoxyethyl(meth)acrylate,
methoxypolyethylene glycol(meth)acrylate,
20 methoxypolypropylene glycol(meth)acrylate, diacetone
(meth)acrylamide, isobutoxymethyl(meth)acrylamide,
N,N-dimethyl(meth)acrylamide, t-octylethyl(meth)acrylamide,
dimethylaminoethyl(meth)acrylate,
diethylaminoethyl(meth)acrylate, 7-amino-3,7-
25 dimethyloctylethyl(meth)acrylate, N,N-diethyl-
(meth)acrylamide, N,N-dimethylaminopropyl-
(meth)acrylamide, hydroxy butyl vinyl ether, lauryl
vinyl ether, cetyl vinyl ether, 2-ethylhexyl vinyl
ether, acrylate monomers shown by the following
30 formulas (3) to (5),



wherein R^2 is a hydrogen atom or methyl group, R^3 is an
alkylene group having 2-6, preferably 2-4, carbon
5 atoms, R^4 is a hydrogen atom, an organic group
containing 1-12 carbon atoms or an aromatic ring, and m
is an integer from 0 to 12, preferably 1-8.



wherein R^2 is the same as defined above, R^3 is an
10 alkylene group having 2-8, preferably 2-5, carbon
atoms, and p is an integer from 1-8, preferably 1-4,



wherein R^2 , R^3 , and p are the same as defined above, and
25 R^6 is a hydrogen atom or methyl group.

Examples of commercially available products
useful as polymerizable monofunctional vinyl monomers
include Aronix M102, M110, M111, M113, M117

(manufactured by Toagosei Co., Ltd.), LA, IBXA, Viscoat #190, #192, #2000 (manufactured by Osaka Organic Chemical Industry Co., Ltd.), Light Acrylate EC-A, PO-A, NP-4EA, NP-8EA, M-600A, HOA-MPL (manufactured by Kyoeisha Chemical Co., Ltd.), and KAYARAD TC110S, R629, R644 (manufactured by Nippon Kayaku Co., Ltd.) can be given.

Examples of useful polymerizable polyfunctional vinyl monomers include the following acrylate compounds: trimethylolpropane tri(meth)acrylate, pentaerythritol tri(meth)acrylate, ethylene glycol di(meth)acrylate, tetraethylene glycol di(meth)acrylate, polyethylene glycol di(meth)acrylate, 1,4-butanediol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, neopentyl glycol di(meth)acrylate, trimethylolpropane trioxymethyl (meth)acrylate, tris(2-hydroxyethyl) isocyanurate tri(meth)acrylate, tris(2-hydroxyethyl) isocyanurate di(meth)acrylate, bis(hydroxymethyl)tricyclodecane di(meth)acrylate, di(meth)acrylate of a diol which is an addition compound of ethylene oxide or propylene oxide to bisphenol A, di(meth)acrylate of a diol which is an addition compound of ethylene oxide or propylene oxide to hydrogenated bisphenol A, epoxy(meth)acrylate obtained by the addition of (meth)acrylate to diglycidyl ether of bisphenol A, diacrylate of polyoxyalkylene bisphenol A, and triethylene glycol divinyl ether.

Examples of commercially available polymerizable polyfunctional vinyl monomers products include Yupimer UV SA1002, SA2007 (manufactured by Mitsubishi Chemical Corp.), Viscoat #195, #230, #215,

#260, #335HP, #295, #300, #700 (manufactured by Osaka Organic Chemical Industry Co., Ltd.), Light Acrylate 4EG-A, 9EG-A, NP-A, DCP-A, BP-4EA, BP-4PA, PR-3A, PE-4A, DPE-6A (manufactured by Kyceisha Chemical Co., Ltd.), KAYARAD R-604, DPCA-20, -30, -60, -120, HX-620, D-310, D-330 (manufactured by Nippon Kayaku Co., Ltd.), and Aronix M-208, M-210, M-215, M-220, M-240, M-305, M-309, M-315, M-325 (manufactured by Toagosei Co., Ltd.).

It is desirable to use these polymerizable diluents in an amount of 10-70 wt%, preferably 15-50 wt%, in the total amount of the resin composition of the present invention. If more than 70 wt%, the resulting cured products may not have sufficiently high toughness.

The ratio by weight of the polymerizable monofunctional vinyl monomer and the polymerizable polyfunctional vinyl monomer in the polymerizable diluent is in the range of 60-100:40-0, and preferably 65-100:35-0. If the ratio of the polymerizable monofunctional vinyl monomer is less than 60 wt%, the Young's modulus of the cured products becomes too high to exhibit characteristics required in the present invention.

The liquid curable resin composition of the present invention can be cured by heat or radiation. Here, radiation includes infrared radiation, visible rays, ultraviolet radiation, X-rays, electron beams, α -rays, β -rays, γ -rays, and the like. The use of UV radiation is preferred.

A polymerization initiator can be added when the liquid curable resin composition of the

present invention is cured. Either a heat polymerization initiator or photo-polymerization initiator can be used as the polymerization initiator.

When the liquid curable resin composition of the present invention is cured by heat, a heat polymerization initiator, usually a peroxide or an azo compound, is used. Specific examples are benzoyl peroxide, t-butyl-oxybenzoate, and azobis isobutyronitrile. It is however preferred to cure the resin composition using radiation.

When the liquid curable resin composition of the present invention is cured by radiation, preferably a photo-polymerization initiator is used. In addition, a photosensitizer is added as required. Given as examples of the photo-polymerization initiator are 1-hydroxycyclohexylphenyl ketone, 2,2-dimethoxy-2-phenylacetophenone, xanthone, fluorenone, benzaldehyde, fluorene, anthraquinone, triphenylamine, carbazole, 3-methylacetophenone, 4-chlorobenzophenone, 4,4'-dimethoxybenzophenone, 4,4'-diaminobenzophenone, Michler's ketone, benzoin propyl ether, benzoin ethyl ether, benzyl methyl ketal, 1-(4-isopropylphenyl)-2-hydroxy-2-methylpropan-1-one, 2-hydroxy-2-methyl-1-phenylpropan-1-one, thioxanethone, diethylthioxanthone, 2-isopropylthioxanthone, 2-chlorothioxanthone, 2-methyl-1-[4-(methylthio)phenyl]-2-morpholino-propane-1-on, 2,4,6-trimethylbenzoyl diphenylphosphine oxide, and bis-(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentyl phosphine oxide.

Examples of commercially available products of the photo-polymerization initiator include

IRGACURE184, 369, 651, 500, 907, CGI1700, CGI1750, CGI1850, CG24-61, Darocur1116, 1173 (manufactured by Ciba-Geigy), Lucirin LR8728 (manufactured by BASF), and Ubecryl P36 (manufactured by UCB).

5 Given as examples of the photosensitizer are triethylamine, diethylamine, N-methyldiethanolamine, ethanolamine, 4-dimethylaminobenzoic acid, methyl 4-dimethylaminobenzoate, ethyl 4-dimethylaminobenzoate, and isoamyl 4-dimethylaminobenzoate. As
10 commercially available products, for example, Ubecryl P102, 103, 104, and 105 (manufactured by UCB) are given. It is however preferred to use no (or a limited amount of) amine group comprising compounds.

 When heat and radiation are used in
15 combination to cure the liquid curable resin composition of the present invention, the foregoing heat polymerization initiator and photo-polymerization initiator can be used in combination. The amount of the polymerization initiator used here is in the range of
20 0.1-10 wt%, and preferably 0.5-7 wt%, in the total amount of the components (1), (2), and (3).

 Beside the above-described components, other curable oligomers or polymers may be added to the liquid curable resin composition of the present
25 invention to the extent that the characteristics of the liquid curable resin composition are not adversely affected.

 Such other curable oligomers or polymers include a polyester (meth)acrylate, epoxy
30 (meth)acrylate, polyamide (meth)acrylate, siloxane polymer having (meth)acryloyloxy group, and a reactive

polymer obtained by reacting (meth)acrylic acid and a copolymer of glycidyl methacrylate and another polymerizable monomer.

An amine compound can be added to the
5 liquid curable resin composition of the present invention to prevent generation of hydrogen gas which causes transmission loss in the optical fibers. As examples of the amine which can be used here, diallylamine, diisopropylamine, diethylamine, and
10 diethylhexylamine can be given.

In addition to the above-described components, various additives, such as antioxidants, UV absorbers, light stabilizers, silane coupling agents, coating surface improvers, heat polymerization
15 inhibitors, leveling agents, surfactants, colorants, preservatives, plasticizers, lubricants, solvents, fillers, aging preventives, and wettability improvers, can be used in the liquid curable resin composition of the present invention, as required.

20 Given as examples of the antioxidants are Irganox1010, 1035, 1076, 1222 (manufactured by Ciba Geigy), Antigene P, 3C, FR, GA-80 (manufactured by Sumitomo Chemical Industries Co., Ltd.); as examples of the UV absorbers, Tinuvin P, 234, 320, 326, 327, 328,
25 329, 213 (manufactured by Ciba Geigy), Seesorb 102, 103, 110, 501, 202, 712, 704 (manufactured by Sypro Chemical Co., Ltd.); as examples of the light stabilizers, Tinuvin 292, 144, 622LD (manufactured by Ciba Geigy), Sanol LS770 (manufactured by Sankyo Co.,
30 Ltd.), Sumisorb TM-061 (manufactured by Sumitomo Chemical Industries Co., Ltd.); as examples of the

silane coupling agent, γ -aminopropyltriethoxysilane, γ -mercaptopropyltrimethoxy-silane, and γ -methacryloxy-propyltrimethoxysilane, and commercially available products such as SH6062, SH6030 (manufactured by Toray-
5 Dow Corning Silicone Co.), and KBE903, KBE603, KBE403 (manufactured by Shin-Etsu Chemical Co., Ltd.); as examples of the coating surface improvers, silicone additives such as dimethylsiloxane polyether and commercially available products such as DC-57, DC-190
10 (manufactured by Dow-Corning Co.), SH-28PA, SH-29PA, SH-30PA, SH-190 (manufactured by Toray-Dow Corning Silicone Co.); KF351, KF352, KF353, KF354 (manufactured by Shin-Etsu Chemical Co., Ltd.), and L-700, L-7002, L-7500, FK-624-90 (manufactured by Nippon Unicar Co.,
15 Ltd.).

The curable resin composition of the present invention is preferably a liquid at 25°C. The viscosity of the liquid curable resin composition of the present invention is usually in the range of 200 to
20 20,000 cp, and preferably 2,000 to 15,000 cp, at 25°C.

The Young's modulus at 23°C of the cured products produced from the liquid curable resin composition of the present invention is preferably 10 kg/mm² or less, more preferably 5 kg/mm² or less, and
25 most preferably 3 kg/mm² or less. Generally, the Young's modulus will be 0.1 kg/mm² or higher, preferably 0.3 kg/mm² or higher.

Moreover, it is desirable that two sheets of cured films made from the liquid curable resin
30 composition of the present invention adhered to each

other has a T-peel strength of 50 g/cm or less, preferably 45 g/cm or less. If the T-peel strength is higher than 50 g/cm, optical fibers adhere to each other or to winding parts of a pulley or the like when
5 optical fibers are manufactured, preventing a smooth operation for the manufacture of optical fibers. The T-peel strength in general will be about 0.5 or higher, preferably 2.5 g/cm or higher.

Cured coatings of the present invention
10 preferably are used as single coatings, secondary coating or ink coatings for optical fibers, preferably optical glass fibers. The coatings are in particular useful as secondary coatings. The secondary coatings can be colored with suitable pigments. Coatings for
15 optical fibers are distinguished by matrix or bundling materials, as coatings cover only one optical fiber, and matrix or bundling material, cover a plurality of coated optical fibers.

The present invention will be explained in
20 more detail by way of examples, which are not intended to be limiting of the present invention. In the examples hereinafter, "part(s) by weight" is simply indicated by "part(s)".

25 Synthetic Example 1

Synthesis of urethane (meth)acrylate of the component (1)

13.5 wt% of tolylene diisocyanate, 0.08 wt% of di-n-butyltin dilaurate, and 0.02 wt% of 2,6-di-t-butyl-p-cresol were placed in a reaction vessel
30 equipped with a stirrer. The mixture was cooled to 5 to

10°C. 9.0 wt% of 2-hydroxyethylacrylate was added dropwise while stirring so as to control the temperature at 10°C or lower. After the addition, the mixture was reacted at 30°C for one hour. Then, 77.5 wt%
5 of polytetramethylene glycol having a number average molecular weight of 2,000 was added and the mixture was reacted for a further 2 hours at 50 to 70°C. The reaction was terminated when the content of the residual isocyanate was 0.1 wt% or less. The urethane
10 acrylate obtained is designated as UA-1.

Synthetic Example 2

Synthesis of urethane (meth)acrylate of the component (1)

15 11.0 wt% of tolylene diisocyanate, 0.08 wt% of di-n-butyltin dilaurate, and 0.02 wt% of 2,6-di-t-butyl-p-cresol were placed in a reaction vessel equipped with a stirrer. The mixture was cooled to 5 to 10°C. 4.9 wt% of 2-hydroxyethylacrylate was added
20 dropwise while stirring so as to control the temperature at 10°C or lower. After the addition, the mixture was reacted at 30°C for one hour. Then, 84.1 wt% of polytetramethylene glycol having a number average molecular weight of 2,000 was added and the mixture was
25 reacted for a further 2 hours at 50 to 70°C. The reaction was terminated when the content of the residual isocyanate was 0.1 wt% or less. The urethane acrylate obtained is designated as UA-2.

Synthetic Example 3Synthesis of polydimethylsiloxane compound of the component (2)

12.0 wt% of tolylene diisocyanate, 79.9 wt% of α -[3-(2'-hydroxyethoxy)propyl]- ω -trimethylsilyl-oxypolydimethyl-siloxane with a hydroxyl group equivalent of 1,200, and 0.02 wt% of 2,6-di-t-butyl-p-cresol were placed in a reaction vessel equipped with a stirrer and the mixture was cooled to 5 to 10°C. When the temperature became 10°C or less, 0.08 wt% of di-n-butyltin dilaurate was added while stirring. The mixture was stirred for one hour while controlling the temperature at 20 to 30°C, then for 2 hours at 40 to 50°C. Next, 8.0 wt% of 2-hydroxyethylacrylate was added and the mixture was reacted for 3 hours at 50 to 70°C. The reaction was terminated when the content of the residual isocyanate was 0.1 wt% or less. The polystyrene-reduced number average molecular weight of the resulting polydimethylsiloxane compound, measured by gel permission chromatography using HLS-8020 manufactured by Tosoh Corp. (hereinafter the same), was 1,800. This liquid resin of polydimethylsiloxane is designated as SA-1.

25 Synthetic Example 4Synthesis of polydimethylsiloxane compound of the component (2)

6.2 wt% of tolylene diisocyanate, 89.6 wt% of α -[3-(2'-hydroxyethoxy)propyl]- ω -trimethylsilyl-oxypolydimethyl-siloxane with a hydroxyl group

equivalent of 2,500, and 0.02 wt% of 2,6-di-t-butyl-p-cresol were placed in a reaction vessel equipped with a stirrer and the mixture was cooled to 5 to 10°C. When the temperature became 10°C or less, 0.08 wt% of di-n-butyltin dilaurate was added while stirring. The mixture was stirred for one hour while controlling the temperature at 20 to 30°C, then for 2 hours at 40 to 50°C. Next, 4.2 wt% of 2-hydroxyethylacrylate was added and the mixture was reacted for 3 hours at 50 to 70°C. The reaction was terminated when the content of the residual isocyanate was 0.1 wt% or less. The polystyrene-reduced number average molecular weight of the resulting polydimethylsiloxane compound was 5200. This liquid resin of polydimethylsiloxane is designated as SA-2.

Examples 1-5. Comparative Examples 1-4

The components listed in Table 1 were charged into a reaction vessel equipped with a stirrer and stirred for 3 hours while controlling the temperature at 50 to 70°C, to obtain liquid curable resin compositions with the formulations shown in Table 1.

Examples

The liquid curable resin compositions prepared in the above examples were cured, and test specimens were prepared and evaluated according to the following methods. The results are shown in Table 1.

1. Measurement of Young's modulus

The liquid curable resin composition was applied to a glass plate using an applicator bar with a thickness of 250 μm and cured by exposure to
5 ultraviolet radiation at a dose of 1 J/cm^2 in the air. The cured product was conditioned at a room temperature of 23°C and a relative humidity of 50% for more than 12 hours to obtain a test specimen. Young's modulus was measured at 23°C according to a method conforming to JIS
10 K7113, provided that the tensile velocity was 1 mm/min and the Young's modulus was calculated from the tensile stress at 2.5% distortion.

2. Measurement of surface property (T-peel strength)

15 The tackiness of the liquid curable resin composition was measured as the T-peel strength. A sample of the liquid curable resin was applied to glass plates using an applicator bar with a thickness of 150 μm and cured with ultraviolet radiation at a dose of
20 0.5 J/cm^2 in the air. Immediately after irradiation, the exposed faces of two sheets of the cured film were placed into contact against each other. A load of 1 kg was imposed on 10 cm^2 area of the films urging the films toward each other for 5 minutes. The contacting sheets
25 were then conditioned at a room temperature of 23°C and a relative humidity of 50% for 6 hours or longer. The contacting sheets were then cut into strips with a width of 2 cm to obtain test specimens. The T-peel strength was measured as the force in g/cm, per 1 cm
30 width, to peel these contacting sheets apart at a

peeling rate of 500 mm/min and 23 °C. The results are shown in Table 1.

3. Measurement of liquid storage stability

5 The storage stability in the liquid state of the resin composition was measured by allowing the composition to stand for 30 days at 60°C, dropping the liquid resin onto a glass plate, and observing the presence or absence of a separated substance on the
10 liquid surface by, unmagnified, visual inspection. The results of the inspection indicated that the composition was stable when there was no separated substance, and unstable when a separated substance was observed.

15 The results of evaluation are shown in Table 1.

Effect of the Invention

20 The liquid curable resin composition of the present invention exhibits excellent stability in the liquid state and produces cured products having low tendency to stick in spite of its low Young's modulus. The composition is suitable for use as a coating material requiring a low Young's modulus.

25

TABLE 1

	Example					Comparative Example			
	1	2	3	4	5	1	2	3	4
Component (1)									
- UA-1	63.9	64.5				63.9	64.5		50.0
- UA-2			65.9	65.9	54.9			65.9	
Component (2)									
- SA-1	1.0		2.0						
- SA-2		0.5		1.0	2.0				
Component (3)									
<u>il monofunctional diluent</u>									
- N-vinylpyrrolidone *1	6.0	6.0	4.0	5.0	5.5	7.0	6.0	6.0	6.0
- Isobornylacrylate *1	20.0	20.0	10.0	10.0	16.5	20.0	20.0	10.0	10.0
- Laurylacrylate *1			10.0	10.0				10.0	
- Compound of formula (3)*1*2					18.00				
- Bis(hydroxymethyl)tricyclo-decanediacylate *3	6.0	6.0	5.0	5.0		6.0	6.0	5.0	31.0
Ratio of *1/*3 (by weight)	01/19	81/19	83/17	83/17	100/0	02/18	82/18	84/16	34/66

	Example					Comparative Example			
	1	2	3	4	5	1	2	3	4
Photopolymerization initiator									
- 1-Hydroxycyclohexyl phenyl ketone	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
Surface improver									
- Graft copolymer of dimethylsiloxane polycarbonol	0.1		0.1	0.1	0.1	0.1	0.5	0.1	
Properties									
- Young's modulus at 23°C (kg/mm ²)		1.2	0.6	0.6	0.3	1.4	1.2	0.6	31
- T-peel strength (g/cm)		5	35	29	43	72	55	90	5
- Liquid storage stability		Stable	Stable	Stable	Stable	Stable	Un-stable	Stable	Stable

*1: polymerizable monofunctional vinyl monomer *2: hydrogen atom; R², alkylene group having 2 carbon atoms,

R³, p-nonylphenyl group, R⁴ *3: polymerizable polyfunctional vinyl monomer

WHAT IS CLAIMED IS:

1. Optical fiber coating, the coating before curing
5 is a curable resin composition comprising:
 (A) at least one urethane (meth)acrylate
 oligomer;
 B) at least one urethane (meth)acryloyl
 polysiloxane compound; and
10 (C) at least one polymerizable vinyl monomer
 diluent.
2. The optical fiber coating according to claim 1,
 wherein the composition comprises, relative to
 the total weight of components (A), (B) and (C):
15 30-80 parts by weight of component (A);
 0.01-10 parts by weight of component (B);
 10-70 parts by weight of component (C).
3. The optical fiber coating according to claims 1
 and 2, wherein the urethane (meth)acryloyl
20 polydimethylsiloxane compound comprises only one
 (meth)acryloyl group.
4. The optical fiber coating according to claims 1-
 3, wherein the composition has a viscosity in the
 range of 200 to 20,000 cp at 25°C.
- 25 5. The optical fiber coating according to claims 1-
 4, wherein the ratio of monofunctional vinyl
 monomer diluent to polyfunctional vinyl monomer
 in the range of 65-100/35-0.
6. The optical fiber coating according to anyone of
30 claims 1-5, wherein the polysiloxane is a
 polydimethylsiloxane.

7. A coated optical fiber having a coating according to any one of claims 1-6.
8. A coated optical fiber of claim 7, wherein the coating is a single coating.
- 5 9. A coated optical fiber of claim 7, wherein the coating is a secondary coating.
10. A coated optical fiber of claim 7, wherein the coating is a colored secondary coating.
11. A coated optical fiber of claim 7, wherein the
10 coating is an ink coating.
12. A coated optical fiber according to any one of claims 7-11 which coating has a Young's modulus of 10 kg/mm² or less at 23°C.
13. A coated optical fiber according to any one of
15 claims 7-12 which exhibits 50 g/cm or less T-peel strength at the interface of two sheets of such films when the two sheets are layered in a way that the cured surfaces of the two films are facing each other.

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/NL 98/00575

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C03C25/02 C08G18/61 C09D4/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C03C C08G C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E	WO 98 46693 A (DSM NV) 22 October 1998 see claims	1-13
X	DATABASE WPI Section Ch. Week 8825 Derwent Publications Ltd., London, GB; Class A28, AN 88-170905 XP002088903 & JP 63 107846 A (NITTO ELECTRIC IND CO) . 12 May 1988 see abstract	1-13



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Patent family members are listed in annex

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/NL 98/00575

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>DATABASE WPI Section Ch, Week 8815 Derwent Publications Ltd., London, GB; Class A25, AN 88-103102 XP002088904 & JP 63 054412 A (NITTO ELECTRIC IND CO) , 8 March 1988 see abstract</p>	1-13
A	<p>DATABASE WPI Section Ch, Week 9127 Derwent Publications Ltd., London, GB; Class A13, AN 91-196941 XP002088905 & JP 03 121411 A (KURARAY CO LTD) , 23 May 1991 see abstract</p>	1
A	<p>EP 0 407 004 A (BORDEN INC.) 9 January 1991 see the whole document</p>	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No.

PCT/NL 98/00575

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